Journal of Alloys and Compounds 722 (2017) 158–165

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Synthesis and significantly enhanced microwave absorption properties of cobalt ferrite hollow microspheres with protrusions/polythiophene composites

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ARTICLE INFO

Article history:
Received 9 March 2017
Received in revised form
1 June 2017
Accepted 3 June 2017
Available online 8 June 2017

Keywords:
Polythiophene
Electromagnetic properties
Microwave absorption

ABSTRACT

Cobalt ferrite hollow microspheres with protrusions/polythiophene (CFHMP/PTh) composites were successfully prepared by in-situ polymerization method of thiophene with CFHMP. The morphology, phase structure, thermal stability, static magnetic and electromagnetic parameters of samples were analyzed and characterized by scanning electron microscope (SEM), X-ray Diffraction (XRD), Fourier transform infrared spectroscopy (FT–IR), thermogravimetric analysis (TG), vibrating sample magnetometer (VSM) and vector network analyzer (VNA). The results indicate that the saturation magnetization (Ms) and remnant magnetization (Mr) and coercivity (Hc) of CFHMP/PTh composites are 566.4 Oe, 40.8 emu/g and 17.6 emu/g, respectively. The dielectric property of CFHMP/PTh composites is better than that of CFHMP, but the magnetic property of CFHMP/PTh composites is worse than that of CFHMP. At the thickness of 3.0 mm CFHMP/PTh composites exhibit strong electromagnetic dissipation ability ($R_L = -33.8$ dB at 9.5 GHz) and the absorption bandwidth ($R_L < -10$ dB) is 3.1 GHz (8.2–11.3 GHz).

1. Introduction

With the development of electronic industry and various electronic devices, electromagnetic radiation has become a new pollutant. Electromagnetic radiation not only affects the proper functioning of a variety of electronic equipment but also is harmful to health [1,2]. Therefore, the study of electromagnetic radiation protection has become a hot spot. The traditional electromagnetic shielding materials achieve the purpose of shielding mainly through the reflection of electromagnetic waves [3]. However, the reflected electromagnetic waves still affect human health and the proper functioning of the external electronic devices. Therefore, it is necessary to develop an electromagnetic shielding material with high absorption and low reflection loss to electromagnetic waves [4].

Ferrites have been utilized as absorbing materials in various forms for many years due to their large magnetic loss and large resistivity ($\rho = 10^{-2} \sim 10^{12}\ \Omega$ cm). The imaginary part of complex permittivity of ferrite is very small. Therefore, the dielectric loss is almost negligible, and their absorbing performance mainly depends on the magnetic loss [5]. However, due to reduced magnetic permeability of ferrites in higher GHz range, resonance absorption is weak, and also in narrow frequency range. Alternatively, ferrites can be engineered to enhance dielectric losses in the wide frequency by appropriate composites [6]. For instance, C.C. Yang fabricated $BaFe_{12}O_{19}$/polyaniline composites, which have good compatible dielectric and magnetic properties. The results indicated that the composites exhibited excellent absorption performances over a broadband range in the radar band (2–40 GHz) with good electromagnetic properties. The $BaFe_{12}O_{19}$/PANI composites showed two absorption bands at 7.8 and 24.2 GHz with −12.5 and −11.5 dB in reflection loss [7].

Ferrite with different morphologies can effect on the magnetic properties including hysteresis loop, specific saturation magnetization and coercivity. It is well known that the specific saturation magnetization belongs to one of intrinsic properties for magnetic materials. It is mainly decided by the structure and components of materials. The coercivity, the susceptibility and the remnant magnetization belong to the extrinsic properties of ferrite. The value of coercivity is not only related to the component of materials, but also decided by their microstructure, such as the grain size, the particle size distribution, agglomeration and defects [8–10]. For instance, Sonal Singhal studied the magnetic properties of $BaAlFe_{11}O_{19}$ hexaferrite with different morphologies. Magnetic

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http://dx.doi.org/10.1016/j.jallcom.2017.06.029
0925-8388/

measurement shows the coercivity of $BaAlFe_{11}O_{19}$ nanosheets (3237 Oe) is higher and the coercivity of the $BaAlFe_{11}O_{19}$ nanoparticles (700 Oe) is lower [10].

Ferrite hollow microspheres as an important branch of the core-shell structure materials are widely concerned by many scholars. Ferrite hollow microspheres not only have all the advantages of ferrite solid microspheres but also have low density, good dispersion, high specific surface, high surface activity, high surface permeability, high stability and other characteristics [11]. The hollow portion can accommodate a large number of guest molecules or large-sized objects, making it important application prospects in the microwave absorbent materials and drug delivery and many other technical fields. For example, Hongfei Lou prepared M-type $BaFe_{12}O_{19}$ hollow ceramic microspheres absorbent. The minimum reflection loss and bandwidth ($R_L < -10$ dB) were −22.1 dB and 5.7 GHz (12.3–18 GHz), respectively [12]. Cong Zhang prepared size-controllable magnetic hollow spheres (MHS). The research indicated that the morphologies and stacking modes of samples affected the microwave absorbing properties [13].

Polythiophene (PTh) and its derivatives have good environmental stability, high electrical conductivity after doping and have higher Seebeck coefficient than other conductive polymers, which are widely used in electronic products, information industry, absorbing materials and other fields [14,15]. Polythiophene as a microwave absorbing material only has dielectric loss. Magnetic-conductive composites with an organized structure usually provide a new functional hybrid, which has synergetic or complementary behavior between magnetic and conductive materials [16]. In order to enhance the absorption properties of polythiophene, it is necessary to adjust its electromagnetic parameters and enhance its magnetic loss. Hence, the research about inorganic magnetic media and conductive polythiophene composites has aroused great concern [17]. For example, S. H. Hosseini successfully synthesized $Ba_xSr_{1-x}Fe_{12}O_{19}/Fe_3O_4$/polyacrylic acid/polythiophene. The microwave-absorbing properties of nanocomposites were investigated at 8–14 GHz. A typical layer absorber exhibited an excellent microwave absorption with a −26 dB maximum absorption at 14 GHz [18].

In order to tune the complex permeability and microwave absorption of ferrite, one of the frequently used methods is to dope the ferrites with metallic ions, such as Cu, Zn, Co, Li, Mg, etc. [19]. In addition, cobalt ferrite ($CoFe_2O_4$) nanocrystals have received a great deal of attention owing to remarkable properties, such as relatively large magnetic anisotropy, good mechanical hardness and chemical stability, and interesting light-induced coercivity change [20,21]. For the above reasons, the sintered ferrite was doped by divalent metal ion Co^{2+} in our work. There are many researches about spherical, rod-shaped, pie-like, hollow spherical ferrite and their composites, but ferrite hollow microspheres with protrusions and their composites are reported less. The purpose of this paper is to study the preparation and microwave absorption performance of polythiophene and cobalt ferrite hollow microspheres with bumps composites. Compared with the previous reports [7,15], this novel absorbing material can improve absorption efficiency, broaden the microwave absorption band and meet the requirements of stealth and electromagnetic compatibility (EMC) technology by adjusting the electromagnetic parameters of materials.

2. Experimental

2.1. Materials

Thiophene monomer, cobaltous nitrate ($Co(NO_3)_2 \cdot 6H_2O$), anhydrous iron (III) chloride ($FeCl_3$), chloroform ($CHCl_3$) were supplied by Shanghai Macklin Biochemical Co., Ltd.. Sodium hydroxide (NaOH), 3-Aminopropyltriethoxysilane (KH-550), ferric nitrate ($Fe(NO_3)_3 \cdot 9H_2O$) were bought from Nanjing Chemical Reagent Co., Ltd.. Polystyrene microspheres (PS) was purchased from Janus New-Materials Co., Ltd.. All reagents were used without further purification.

2.2. Surface treatment of PS

There are residual oily substances as well as some residual groups on the surface of PS, which can affect the deposition of ferrite on the surface of PS and uniformity of the deposited layer. Meanwhile, the smooth and inert surface of PS is not conducive to the ferrite's deposition. So its surface is sulfonated and roughened to obtain sulfonic acid groups. The reaction process is as follows:

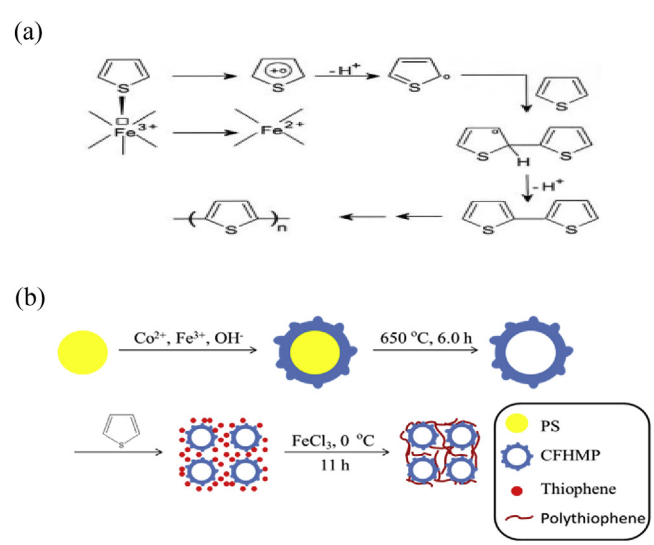
Typically, 3 g PS was dispersed in 50 mL ethyl alcohol under ultrasonic for 30 min, and then was centrifuged, washed with ethanol several times and dried at 50 °C in air. Then, PS was put into 50 mL of concentrated sulfuric acid under gentle stirring at 20 °C for 12 h, filtered, washed with deionized water and dried in a vacuum.

2.3. Preparation of cobalt ferrite hollow microspheres with protrusions

The synthesis of cobalt ferrite hollow microspheres with protrusions (CFHMP) was divided into two steps, as shown in Scheme 1. Firstly, PS (0.4 g), $Co(NO_3)_2 \cdot 6H_2O$ (2.4809 g) and $Fe(NO_3)_3 \cdot 9H_2O$ (6.8878 g) were added to 50 mL of deionized water and sonicated for 30 min. Then, the sodium hydroxide solution (3 M) was added dropwise to the above suspension until the pH was equal to 12 [22]. The mixture was stirred at 80 °C for 4.0 h. The resulting product was filtered, washed with deionized water and dried in air. Secondly, CFHMP was obtained through calcining above precursor particles at 650 °C (heating rate: 10 °C/min) for 6.0 h [23].

2.4. Preparation of CFHMP/PTh composites

A typical procedure for preparing CFHMP/PTh composites was described as follows: CFHMP (1.0 g) was firstly pretreated with KH550 (2.0 g). The pretreated CFHMP was added into 50 mL $CHCl_3$ containing $FeCl_3$ (3.8554 g) and then carried out ultrasonic treatment for 1.0 h at room temperature. Then, thiophene monomer



Scheme 1. Proposed mechanism of thiophene in situ polymerization with $FeCl_3$ in $CHCl_3$ (a) and schematic illustration of the process for the synthesis of CFHMP/PTh composites (b).